GIBBS FREE ENERGY OF FORMATION OF HYDRATED AND DEHYDRATED CLAY MINERALS

TARDY Y.

Institut Francais de Recherche Scientifique pour le Développement en Coopération
ORSTOM, BP 2528, Bamako, Mali.
Institut de Géologie, Université Louis Pasteur, 1,rue Blessig, 67084 Strasbourg, France.

INTRODUCTION

Clay minerals are hydrated in common natural earth surface conditions. Water is distributed in five different sites : (i) structural sites where water is represented by hydroxyls (OH) part of structures, (ii) interlayer water attached to interlayer cations between individual layers, (iii) intra-particle water attached to surfaces in intermediate position between groups of layers within a given particle, (iv) inter-particle sites at the surface of individual particles, (v) inter-agregate water poorly attached to the surfaces of agregates made of assemblages of particles. Structural water is supposed so strongly linked to the crystalline framework that it should not be affected by changes in environment conditions Consequently what is called a dehydrated clay mineral includes its OH-hydroxyls.

There are still some people who consider that hydration water only concerns inter-layer sites. Recent works have shown that hydration of clay minerals involves not only interlayer sites but also intra- and inter-particle sites as well as inter-agregate sites (TOURET, 1988). The total amount of hydration water and the relative amounts of the different types of hydration water are fluctuating depending on the environment parameters such as temperature, external pressure, degree of compaction, salinity of the surrounding solution in which clay minerals tend to equilibrate. This work shows how the Gibbs free energy of formation of clay minerals and consequently their stability field change as function of their degree of hydration.

GIBBS FREE ENERGY OF HYDRATION

The Gibbs free energy of formation of a given hydrated clay mineral can be calculated as follows (see BARSHAD, 1955; TARDY et al. , 1980; GARRELS and TARDY, 1982; TARDY and TOURET, 1987) :

$$\Delta G°_f \text{ (hydrated clay)} = \Delta G°_f \text{ (dry clay)} + \Delta G \text{ (hydration)} + n \Delta G°_f(H_2O) \qquad (1)$$

In this reaction n stands for the number of water molecules involved per one mole of dry clay. ΔG(hydration) is obtained by integrating along the dehydration isotherm the following function :

$$\Delta G \text{(hydration)} = RT \int_0^n Ln \, a_w \, dn \qquad (2)$$

In this equation a stands for the activity of water. In our convention, the standard state of water ($a_w = 1$) is defined when water is pure and at a total pressure of 1bar = 10^5Pa. In standard state the Gibbs free energy of water is written as $\Delta G°_f(H_2O)$. Water in hydrated sites of clay minerals is under a pressure lower than the unity even if the total external bulk pressure is strictly equal to 1 bar.

Consequently the activity of water (aw<1) is smaller than one, the Gibbs free energy of hydration is negative, and hydration water is more stable than the pure bulk liquid water. This case is similar to that of gypsum in for example : $CaSO_42H_2O + H_2O$ liquid, where two molecules of hydrated water remain attached to $CaSO_4$ in presence of liquid water. In clay minerals the number of attached water is continuously variable instead to be fixed as in hydrates or gypsum .

Thermodynamic properties of hydration water are close to these of water in hydrates. Molar volume of

hydration water tends to be smaller than this of liquid water, so that clay minerals tend to remain hydrated when pressure increases. Entropy and heat capacity are often smaller than these of liquid water so that an increase of temperature tends to induce dehydration (TARDY et al., 1980).

Gibbs free energy of hydration of a phyllosilicate layer depends on several parameters such as (i) particle size, (ii) layer charge, (iii) nature of the layer charge (tetrahedral or octahedral), (iv) nature of the interlayer cation (Li, Na, K, Ca, Mg) and nature of the octahedral cation (Mg, Fe trioctahedral or Al and Fe dioctahedral). A model to calculate the Gibbs free energy of formation from the elements of a given mineral can be based on an ideal solid solution mixing involving a large number of end members for which Gibbs free energies are estimated. These end members are 4 for talc-pyrophyllite series, 4 for phlogopite-muscovite series, 4 in the celadonite series = 8 in total for

potassium in interlayers time 5 for 5 different interlayer cations, time 2 for hydrated or dehydrated stages so that one can consider about 84 end members.

GIBBS FREE ENERGIES OF HYDRATED AND DEHYDRATED CLAY MINERALS

Giggs free energies of the different hydrated and dehydrated end members were estimated by TOURET (1988). Several data are represented in tables 1 and 2.

Data of table 3 show as an example what are the Gibbs free energy differences between Na- or K- saturated , hydrated or dehydrated clay minerals i.e. between poorly crystallized micas, hydrated or not.

TABLE 1 : Gibbs free energies of formation from the elements (ΔG^{o}_{f}, kJ/mol) (1), Gibbs free energies of formation from the constituent oxides (ΔG^{o}_{ox}, kJ/mol) (2), and solubility products (log K_{sp}) (3) of well crystallized phyllosilicates. Doted values (*) are estimated from the ΔO^{2} method of TARDY and GARRELS (1976, 1977) and TARDY (1982).

TABLE 2 : Gibbs free energies of lormation from the elements (ΔG^{o}_{f}, kJ/mol) [(I) and 2)], Gibbs free energies of formation from the constituent oxides (ΔG^{o}_{ox}, cJ/mol) [(3) and (4) 1 and solubility products (log K_{sp}) [(5) and (6)] of poorly crystallized and hydrated clay minerals. Values listed in columns (1), (3) and (5) are those of FRITZ (1981) modified by TARDY et al. (1986). Values listed in columns (2), (4) and (6) are ajusted to fit the ΔG^{o}_{ox} - ΔO_{2} linear relationship of TARDY and GARRELS (1976, 1977).

	ΔG^{o}_{f}	ΔG^{o}_{ox}	log K_{sp}	ΔG^{o}_{f}		ΔG^{o}_{ox}		log Ksp	
	(1)	(2)	(3)	(1)	(2)	(3)	(4)	(5)	(6)
Mg3 Si4 10 (OH)2	- 5524.9	- 168.3	21.6	- 5504.4	- 5504.4	- 147.8	- 147.8	25.16	25.16
Fe3 Si4 10 (OH)2 .	- 4479.0	- 76.4	7.2	- 4479.0	- 4475.6	- 76.4	- 73.0	7.24	7.83
Al2 Si4 10 (OH)2	- 5256.3	- 25.1	1.1	- 5256.7	- 5267.2	- 25.5	- 36.0	1.00	- 0.84
Fe2 Si4 10 (OH)2	- 4348.7*	+ 42.5*	- 9.8	- 4371.2	- 4371.2	+ 20.0	+ 20.0	- 13.70	- 13.70
K Mg3 Al Si3 10 (OH)2	- 5842.1	- 389.7	38.2	- 5821.1	- 5821.1	- 368.7	- 368.7	41.91	41.91
K Fe3 Al Si3 10 (OH)2	- 4800.3	- 301.9	23.2	- 4799.8	- 4797.5	- 301.4	- 299.1	23.27	23.67
K Al2 AlSi3 10 (OH)2	- 5591.6	- 264.5	14.6	- 5579.6	- 5591.1	- 252.6	- 264.1	16.65	14.65
K Fe2 AlSi3 10 (OH)2	- 4685.5*	- 198.5*	3.5*	- 4699.1	- 4699.1	- 212.1	- 212.1	1.09	1.09
K Mg2.5 Si4 10 (OH)2	- 5569.0*	- 336.0*	23.5*	- 5549.4	- 5549.4	- 316.4	- 316.4	26.93	26.93
K Fe2-5 Si4 10 (OH)2	- 4699.0*	- 261.0*	11.3*	- 4696.3	- 4696.0	- 258.3	- 258.0	11.75	11.80
K Al 1.667 Si4 10 (OH)2	- 5353.0*	- 225.0*	5.0*	- 5345.2	- 5357.2	- 217.2	- 229.2	6.35	4.25
K Fe 1.667 Si4 10 (OH)2	- 4595.3*	- 167.0*	- 3.7*	- 4613.7	- 4613.9	- 185.4	- 185.6	- 6.97	- 7.00

TABLE 3 : Gibbs free energy of hydration of Na-X micas (kJ/mol) (1). Gibbs free energies of formation from the elements (kJ/mol) of various clay micas at 298.15 K and 1 bar total pressure : K-X hydrated (2); Na-X hydrated (3); Na-X dehydrated (4); K-X dehydrated (S) and difference (4) - (5) = (6).

Clay Minerals	ΔG^O hydrat. (1)	ΔG^O_f K-X hyd. (2)	ΔG^O_f Na-X hyd. (3)	ΔG^O_f Na-X dehy. (4)	ΔG^O_f K-X dehy. (5)	Diff. (6)=(4)-(5) (6)
Na Mg3 Al Si3 O10(OH)2	- 21	- 5821.1	- 5795.9	- 5774.9	- 5811.1	+ 36.2
Na Fe3 Al Si3 O10(OH)2	- 21	- 4797.5	- 4772.3	- 4751.3	- 4814.5	+1 63.2
Na Al2 Al Si3 O10(OH)2	- 21	- 5591.1	- 5565.9	- 5544.9	- 5621.1	+ 76.2
Na Fe2 Al Si3 O10(OH)2	- 21	- 4699.1	- 4673.9	- 4652.9	- 4749.1	+ 96.2
Na Mg2 5 Si4 O10(OH)2	- 190	- 5549.4	- 5524.2	- 5334.2	- 5362.4	+ 28.2
Na Fe2.5 Si4 O10(OH)2	- 125	- 4696.0	- 4670.8	- 4545.8	- 4597.0	+ 51.2
Na Al1.667 Si4 O10(OH)2	- 95	- 5357.2	- 5332.0	- 5237.0	- 5307.2	+ 70.2
Na Fe1.667 Si4 O10(OH)2	- 43	- 4613.9	- 4588.7	- 4545.7	- 4641.9	+ 96.2

CONCLUSIONS

The ideal solid solution model of mixing of a large number of hydrated and dehydrated end members seems to be the easiest way to estimate Gibbs free energies of formation of clay minerals of complex and various formulas.

Gibbs free energy of formation of hydrated and dehydrated end members saturated by various interlayer cations are estimated from data on hydration energies as well as from data on cation exchange constants.

In standard earth surface conditions clay minerals are hydrated. They tend to dehydrate in saline water in which the activity of H_2O is small and in diagenetic or metamorphic conditions in which temperatures are high. Thus temperature is perhaps the dominant factor of compaction of shales and clay mineral geological series.

Hydration energies of interlayer cations are depending on the nature of the layer and on the crystal size. Higher the layer charge higher the hydration energies (this is true for most of the clay minerals but not for all). Higher the size and crystallinity smaller the hydration energy. Dioctahedral minerals exhibit smaller hydration energies than trioctahedral phyllosilicates. Most of celadonitic layers octahedrally charged exhibit higher hydration energy than tetrahedrally charged micas.

Sodium is generally more hydrated than potassium and magnesium more hydrated than calcium.

Hydration energy increases with layer charge except for K-saturated aluminous or ferric phyllosilicates such as K-beidellite to muscovite or K-nontronite to glauconite. In these cases it seems that minerals of small size are more stable, in water than minerals of large size. It probably explain why illites and glauconites are of small size and why vermiculites of large size derive more often from phlogopite than from muscovite.

Hydration tends to stabilize cations in interlayer situation. For example, the exchange constant between Na- and K- saturated clay is small when layers are hydrated but high when layers are dehydrated : potassium is much more preferred than sodium in dehydrated conditions or at high temperatures. I consequently believe that the driving force for the transformation of smectite to illite in diagenesis is simply a dehydration reaction due to an increase of temperature, the consequences of which are the chemical transformations observed.

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